

## REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1-14 in the underlying PCT Application No. PCT/DE03/01034 and adds new claims 15-36. The new claims, inter alia, conform the claims to United States Patent and Trademark Office rules and does not add any new matter to the application.

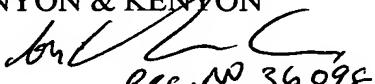
In accordance with 37 C.F.R. § 1.125(b), the Substitute Specification (including the Abstract) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to United States Patent and Trademark Office rules or to correct informalities. No new matter has been added. As required by 37 C.F.R. §§ 1.121(b)(3)(ii) and 1.125(c), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) are respectfully requested.

The underlying PCT Application No. PCT/DE03/01034 includes an International Search Report, dated August 25, 2003, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

It is respectfully submitted that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

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## GLASS-CERAMIC COMPOSITE MATERIAL, CERAMIC SUBSTRATE LAMINATE OR MICROHYBRID HAVING THIS COMPOSITE AND A METHOD FOR PRODUCING IT

FIELD OF THE INVENTION

The present invention relates to a glass-ceramic composite material, a ceramic substrate, a ceramic laminate or a microhybrid having this ceramic composite material, as well as a method for 5 producing the composite material or component parts having it, ~~according to the generic parts of the independent claims.~~

Background Information10 BACKGROUND INFORMATION

Substrate materials for LTCC applications ("low temperature co-fired ceramics") have been developed in the past few years, above all with the aim of reducing the sintering temperature, in order to make possible co-firing, that is, sintering of the entire 15 composite material in one step, with low-melting metals, such as silver. In this context, the compatibility with the metal should be ensured at the same time. It was also an aim to improve the dielectric properties of the LTCC substrate, especially for applications in the high frequency range, and to increase their 20 heat conductivity with regard to heat dissipation from the LTCC substrates.

A glass-aluminum nitride composite material is known from described in European Patent No. EP 0 499 865 A1, which has a comparatively 25 high heat conductivity at a low sintering temperature, and has good dielectric properties. This composite material starts from a glass powder having silicon dioxide, aluminum oxide, boron oxide and an alkaline earth metal oxide such as MgO, CaO or SrO, to which aluminum nitride is added as a ceramic powder component. Upon 30 sintering the starting mixture to the composite material according to described in European Patent No. EP 0 499 865 A1, if MgO is used,

cordierite is formed, and if CaO is used, anorthite is formed, while the glass matrix becomes impoverished in silicon, magnesium and aluminum.

5 SUMMARY

It was the ~~An~~ object of the present invention is to make available a glass-ceramic composite material, especially a substrate material for LTCC applications, which is able to be processed to a ceramic substrate and is able to be used in a ceramic laminate 10 or in a microhybrid, and which has a high overall heat conductivity, if possible in the range of 8 W/mK to 12 W/mK.

Summary of the Invention

15 The glass-ceramic composite material according to an example embodiment of the present invention has the advantage, compared to the related art, that it is ~~may~~ very suitable as a substrate material for LTCC substrates and for the construction of microhybrids having such substrates, and ~~that it particularly has~~ may have a clearly increased heat conductivity, especially in the favorable range of 8 W/mK to 12 W/mK, compared to the usual LTCC substrate materials, whose heat conductivity usually lies between 2 W/mK to 3 W/mK. In this way, the number of required heat dissipations, which are designed in the case of microhybrids, as 20 25 a rule, as thermal lead-throughs, or so-called "thermal vias", i.e., channels filled with a metal that cross the substrate, may be reduced. Thereby comes about the possibility of clearly reducing the size of such microhybrids and of increasing the layout density.

30 A ceramic laminate produced using the glass-ceramic composite material according to the present invention, or a microhybrid based on an LTCC substrate having this glass-ceramic composite material, consequently offers the possibility of saving on thermal vias and of achieving a greater integration density. Finally, silver, that 35 is usually used for filling the thermal vias, will also be saved in part by reducing their numbers.

~~Advantageous further refinements of the present invention result from the measures indicated in the dependent claims.~~

Thus, ~~it is~~ It may be especially advantageous if the ceramic filler is aluminum nitride having an average powder particle size of 100 nm to 10  $\mu\text{m}$ , especially from 1  $\mu\text{m}$  to 10  $\mu\text{m}$ . In this context, the filler may be uncoated aluminum nitride that has an average particle size such as 1  $\mu\text{m}$  to 3  $\mu\text{m}$ , preferably, coated aluminum nitride having an average particle size such as 6  $\mu\text{m}$  to 7  $\mu\text{m}$ , the coating being preferably a hydrophobic surface modification or an oxygen-containing surface coating. ~~It is~~ may be particularly advantageous if the aluminum nitride powder used, especially because of the oxygen-containing surface coating, has an oxygen content of 0.5 wt. % to 2.0 wt. %, it being generally accepted that a lower oxygen content leads to an increased heat conductivity of the aluminum nitride-ceramic powder used.

In addition ~~it is of advantage~~ may be advantageous if the matrix has as the crystalline phase a Li-Al-Si<sub>2</sub>O<sub>3</sub> mixed crystal and/or an Li-Al-Si oxynitride and/or an Li-Al silicate and/or a lithium silicate as the crystalline phase as well as being further made up of a residual glass phase in which nitrogen is soluble at least in small proportions. It is of especial advantage if the matrix contains no lithium silicate, if possible, or as little of it as possible. Furthermore, ~~it is~~ may be advantageous if B<sub>2</sub>O<sub>3</sub> is also put into the starting mixture, so that, at least from place to place, an Li-B oxide may be created as crystalline phase in the matrix.

The proportion of the ceramic fillers in the composite material is preferably between 25 vol. % and 70 vol. %, especially 30 vol. % to 50 vol. %. It is particularly simple to set a heat conductivity in the range aimed for of 8 W/mK to 12 W/mK via the filler proportion.

35 ~~Brief Description of the Drawing~~

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be explained in more detail with reference to the drawingsfigure and in the description below.

Figure 1 shows a top view of a microhybrid having an LTCC substrate as the ceramic substrate.

#### Exemplary Embodiments

#### DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS

Figure 1 shows a microhybrid ~~5 known in principle~~,<sup>5</sup>, having a ceramic substrate 10 in the form of an LTCC foil or an LTCC laminate, substrate 10 having, from place to place, thermal lead-throughs 14, so-called "thermal vias", which cross substrate 10 and which are filled with a metal, for example, silver. Furthermore, electrical lead-throughs 11, so-called "electrical vias", that cross the substrate 10, are provided, whereby printed circuit traces running on the upper side of substrate 10 are able to be contacted from the lower side of substrate 10. Finally, on the upper side of substrate 10 there is shown, as an example, a printed-on resistor 13 that is also connected to the printed-on printed circuit traces 12.

The ~~erux~~ of the present invention ~~is~~ relates to ~~make~~making available a glass-ceramic composite material for producing substrate 10 according to Figure 1.

For this, one first melts a glass from a starting mixture having 20 wt. % to 68 wt. %  $\text{SiO}_2$ , 10 wt. % to 25 wt. %  $\text{Al}_2\text{O}_3$ , 5 wt. % to 25 wt. %  $\text{Li}_2\text{O}$ , 0 wt. % to 33 wt. %  $\text{B}_2\text{O}_3$ , 0 wt. % to 10 %  $\text{P}_2\text{O}_5$ , 0 wt. % to 10 wt. %  $\text{Sb}_2\text{O}_3$  and 0 wt. % to 3 wt. %  $\text{ZrO}_2$ .

Preferably, the starting mixture is made up of 48 wt. % to 66 wt. %  $\text{SiO}_2$ , 14 wt. % to 22 wt. %  $\text{Al}_2\text{O}_3$ , 4 wt. % to 20 wt. %  $\text{Li}_2\text{O}$ , 0 wt. % to 20 wt. %  $\text{B}_2\text{O}_3$ , 0 wt. % to 5 wt. %  $\text{P}_2\text{O}_5$ , 0 wt. % to 5 wt. %  $\text{Sb}_2\text{O}_3$  and 0 wt. % to 2 wt. %  $\text{ZrO}_2$ .

In the case of the components  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{ZrO}_2$ , these are especially preferably added in a proportion of 3 wt. % to 20 wt. %

B<sub>2</sub>O<sub>3</sub> and/or 2 wt. % to 5 wt. % P<sub>2</sub>O<sub>5</sub> and/or 1 wt. % to 5 wt. % Sb<sub>2</sub>O<sub>3</sub> and/or 1 wt. % to 2 wt. % ZrO<sub>2</sub>.

Within the scope of a first exemplary embodiment, the starting mixture is made up of 65 wt. % SiO<sub>2</sub>, 15 wt. % Al<sub>2</sub>O<sub>3</sub> and 20 wt. % Li<sub>2</sub>O.

Within the scope of a second exemplary embodiment, the starting mixture is made up of 65 wt. % SiO<sub>2</sub>, 15 wt. % Al<sub>2</sub>O<sub>3</sub>, 12 wt. % Li<sub>2</sub>O and 8 wt. % B<sub>2</sub>O<sub>3</sub>.

In a third exemplary embodiment, the starting mixture is made up of 50 wt. % SiO<sub>2</sub>, 16 wt. % Al<sub>2</sub>O<sub>3</sub>, 12 wt. % Li<sub>2</sub>O and 20 wt. % B<sub>2</sub>O<sub>3</sub>.

In a fourth exemplary embodiment, the starting mixture is made up of 65 wt. % SiO<sub>2</sub>, 21 wt. % Al<sub>2</sub>O<sub>3</sub>, 4 wt. % Li<sub>2</sub>O, 4 wt. % B<sub>2</sub>O<sub>3</sub>, 4 wt. % P<sub>2</sub>O<sub>5</sub> and 2 wt. % ZrO<sub>2</sub>.

During the production of the glass from this starting mixture, a matrix is created that contains lithium, silicon, aluminum and oxygen, and which, from place to place, has at least one crystalline phase. This crystalline phase is, for instance, an Li-Al-Si<sub>2</sub>O<sub>3</sub> mixed crystal, an Li-Al-Si oxynitride, a lithium silicate or a plurality of such crystalline phases. The non-crystalline regions of the matrix further form a residual glass phase in which, in a small proportion, nitrogen is soluble.

For the production of the above-named glasses, ~~first of all~~ the powder components used in the starting mixture are homogenized and melted at temperatures between 1200° C and 1600° C. After homogenization of the melt, this is then, for example, poured off into water, that is, it is shredded (crackled), and the glass thus obtained is milled down to an average grain size of 1 µm to 5 µm, for instance, 3 µm. After that, to this glass powder there is added, as ceramic filler, powdery aluminum nitride, having an average particle size of 100 nm to 10 µm, preferably 1 µm to 10 µm.

Within the scope of a first exemplary embodiment for producing the glass-ceramic composite material from the glass powder and the ceramic filler, one of the previously described glass powders and, as the ceramic filler, aluminum nitride powder, are homogenized  
5 in an organic solvent such as isopropanol, the powder mixture thus obtained is first dried, and is subsequently submitted to molding, such a uniaxial pressing.

After that, the pressed element obtained is sintered in air, 10 nitrogen or a gas mixture containing oxygen and/or nitrogen at temperatures of at most 1050° C, so that one obtains thereafter a densely sintered glass-ceramic composite material in which, in a glass-type matrix, which from place to place has crystalline phases, the ceramic aluminum nitride particles are embedded.  
15

On this glass-ceramic composite material, with the aid of the "hot disk method", the heat conductivity was then determined. In this context, it was shown that the latter is a function of the proportion of the added ceramic filler.  
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Thus, in the case of a glass having 65 wt. %  $\text{SiO}_2$ , 15 wt. %  $\text{Al}_2\text{O}_3$  and 20 wt. %  $\text{Li}_2\text{O}$  in the starting mixture for producing the glass and a proportion of 70 vol. % of this glass and 30 vol. % aluminum nitride particles in the glass-ceramic composite material, a heat 25 conductivity of 9.1 W/mK was determined, and at a proportion of 65 vol. % of this glass and 35 vol. % of the aluminum nitride particles a heat conductivity of 8.9 W/mK was determined, and at 60 vol. % of this glass and 40 % vol. % of the aluminum nitride particles a heat conductivity of 12.5 W/mK was determined.  
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It has generally been shown that the heat conductivity rises in the glass-ceramic composite material with increasing proportion of aluminum nitride.  
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The stagnant value of the heat conductivity at a composition of 65 vol. % glass and 35 vol. % aluminum nitride is attributed to the high proportion of crystalline lithium silicate formed.

Therefore it is favorable if the glass-ceramic composite material contains as little as possible or no lithium silicate.

5 Testing for crystalline phases within the matrix of the glass-ceramic composite material and the verification of these phases, by the way, was done by X-ray diffractometry and scanning electron microscopy.

10 For the production of a ceramic foil, a ceramic laminate or a microhybrid 5 using substrate 10 made of the above-described glass-ceramic composite material, there is first produced one of the glasses described, it is ground down to the grain size described, and mixed with the described ceramic filler aluminum nitride. Thereafter, there is added to the powder mixture preferably 15 additional, ~~known per se~~conventional components such as a solvent, an organic binding agent, as well as preferably also a dispersing agent, and then one carries out the forming of the mixture, especially to a foil, a layer or a laminate. After forming, first, preferably the binder is removed, and then the foil, layer or 20 laminate is sintered at at most 1050° C in air, nitrogen or a gas mixture containing oxygen and/or nitrogen. In this way, the added binder and the solvent as well as the dispersing agent are at least to a great extent removed again by pyrolysis, so as to create a glass-ceramic-composite material in the desired shape that is free 25 from these temporary components. On the exemplary foil thus produced, which is used as substrate 10 for microhybrid 5, the latter is then constructed in the usual manner for this design layout technology.

AbstractABSTRACT

A glass-ceramic composite material is proposed, described having a matrix that is at least from place to place of a glass type, and 5 having a ceramic filler as well as a ceramic foil, a ceramic laminate or microhybrid (5)—using this composite material, the matrix containing lithium, silicon, aluminum and oxygen, and has at least from place to place a crystalline phase. In addition, a method is proposeddescribed for producing it, a glass having 10 crystalline regions being melted from a starting mixture having 20 wt. % to 68 wt. %  $\text{SiO}_2$ , 10 wt. % to 25 wt. %  $\text{Al}_2\text{O}_3$ , 5 wt. % to 20 wt. %  $\text{LiO}_2$ ,  $\text{Li}_2\text{O}$ , 0 wt. % to 35 wt. %  $\text{B}_2\text{O}_3$ , 0 wt. % to 10 %  $\text{P}_2\text{O}_5$ , 0 wt. % to 10 wt. %  $\text{Sb}_2\text{O}_3$  and 0 wt. % to 3 wt. %  $\text{ZrO}_2$  and converted 15 into a glass powder, a ceramic filler, particularly powdered aluminum nitride, being then mixed in with the glass powder, and this powder mixture is finally sintered, especially after the addition of further components.

Figure-1

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